CLAIMS

1. A mutant form of a glycosidase enzyme, said enzyme being selected from among glycosidase enzymes having two catalytically active amino acids with carboxylic acid side chains within the active site of the wild-type enzyme including a catalytically active amino acid acting as an acid, base, or acid/base catalyst, said mutant enzyme being mutated to replace the catalytically active amino acid acting as an acid, base or acid/base catalyst with a different amino acid having a non-carboxylic acid side chain.

2. The enzyme of claim 1, wherein the different amino acid has a side chain that is approximately equal in size to or smaller than the smaller chain of the replaced amino acid.

3. The enzyme of claim 1 or 2, wherein the different amino acid is selected from the group consisting of alanine, glycine, valine, leucine, isoleucine, serine, threonine, cysteine, methionine, asparagine, glutamine, histidine, proline, phenylalanine, and tyrosine.

4. The enzyme of any of claims 1-3, wherein the mutant enzyme is formed by replacing the amino acid in the active site of an enzyme selected from the group consisting of β-glucosidases, β-galactosidases, β-mannosidases, β-N-acetyl glucosaminidases, β-N-acetyl galactosaminidases, β-xylosidases, β-fucosidases, cellulases, xylanases, galactanases, mannanases, hemicellulases, amylases, glucoamylases, α-glucosidases, α-galactosidases, α-mannosidases, α-N-acetyl glucosaminidases, α-N-acetyl galactosaminidases, α-xylosidases, α-fucosidases, and neuraminidases/sialidases.

5. The enzyme of any of claims 1-3, wherein the mutant enzyme is a mutant of *Agrobacterium* β -glucosidase.

6. The enzyme of claim 5, wherein the mutant enzyme is selected from the group consisting of Abg E171A, E171G, E171Q, E171S, E171T, E171M, E171F, E171L, E171I, and E171N.

7. The enzyme of any of claims 1-3, wherein the mutant enzyme is a mutant of an endo-acting retaining β-glycosidase of *Cellulomonas fimi.*

8. The enzyme of claim 7, wherein the mutant enzyme is Cex E127A.

9. The enzyme of any of claims 1-3, wherein the mutant enzyme is a mutant of an endo-mannanase Man26A of *Cellvibrio japonicus.*

10. The enzyme of claim 11, wherein the mutant enzyme is Man26A E212A.

11. A method for synthesizing a thioglycoside having the structure A-S-B, wherein S is sulfur and A and B are each sugar moieties, comprising the steps of:

(a) combining a donor molecule A-X, where X is a leaving group, and an acceptor molecule HS-B in a reaction mixture; and

(b) enzymatically coupling the donor molecule to the acceptor molecule using a mutant form of a glycosidase enzyme in accordance with any of claims 1-10 to form the thioglycoside.

12. The method of claim 11, wherein the leaving group X is dinitrophenol.

13. The method of claim 11, wherein the donor is selected from the group consisting of 2,4-dinitrophenyl β-D-glucopyranoside (DNP-Glc); 2,5-dinitrophenyl β-D-mannopyranoside (DNP-Man); DNP β-cellobioside , pNP 4'-deoxy-4'-thio-β-cellobioside and β-D-glucosyl azide.

14. The method of any of claims 11 to 13, wherein the acceptor is selected from the group consisting of para-nitrophenyl 4-deoxy-4-thio-β-D-glucopyranoside, para-nitrophenyl 4-deoxy-4-thio-β-D-galactopyranoside; methylumbelliferyl 4-deoxy-4-thio-β-D-glucopyranoside, 4'-deoxy-4'-thio-cellobiose, pNP 4'-deoxy-4'-thio-β-cellobioside, and pNP β-D-4-deoxy-4-thio-glucopyranoside..

15. The method of any of claims 11 to 14, wherein the glycosidase enzyme is a stereochemistry inverting enzyme in which one of the carboxylic acid side chains in the active site functions as an acid catalyst and the other carboxylic acid side chain functions as a base catalyst, and wherein the amino acid having the carboxylic acid side chain which functions as an acid catalyst is replaced in the mutant enzyme.

16. The method of any of claims 11 to 14, wherein the glycosidase enzyme is a stereochemistry retaining enzyme in which one of the carboxylic acid side chains in the active site functions as an acid/base catalyst and the other carboxylic acid side chain functions as a nucleophile, and wherein the amino acid having the carboxylic acid side chain which functions as an acid/base catalyst is replaced in the mutant enzyme.

17. A thioglycoside prepared by the method of any of claims 11 to 16.

18. A fusion protein comprising a mutant form of a glycosidase enzyme according to any of claims 1-10 and a binding element for immobilization of the fusion protein on a solid support.

19. The fusion protein of claim 18, wherein the binding element is the cellulose-binding domain of a *Cellulomonas fimi* exoglucanase.